

Research Article

Aqueous Synthesis and Characterization of CdSe/ZnO Core-Shell Nanoparticles

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Core-shell nanomaterials based on CdSe as the core and ZnO as the shell were prepared using an aqueous route involving the use of Cd salt and NaBH₄ in reaction with Se to generate CdSe in the presence of thioglycerol (TG) as a stabilizer. ZnO has been prepared at pH 12 using stronger base such as NaOH at lower concentration and by varying amounts of Zn²⁺ ions ranging from 2.5, 5, 25 mL, and 50 mL to prepare core-shell nanomaterials. The absorption and emission spectral features are dominated by CdSe nanoparticles with typical shift in the emission maxima red-shifted in relation to the band edges. There is an observable change in the band edge from the core as the amount of ZnO is increased. The TEM features showed the formation of the core-shell from the volume of 5 mL which is indicated by the thin layer of shell on the surface of the CdSe core.

1. Introduction

Core-shell nanocrystals are nanostructures composed of at least two materials in an onion-like structure with the size range of 20–200 nm [1, 2]. Core-shell nanomaterials based on semiconductor cores coated by an oxide shell are very interesting especially for biological and industrial applications [3, 4]. Bare CdSe and other II-IV semiconductor nanocrystals have potential applications in optoelectronic devices due to their tuneable emission colors which depend on the nanoparticle sizes. However, CdSe nanoparticles are unstable as they suffer from photo-oxidation when exposed to air and light [5]. Bare CdSe NCs also suffer from low quantum yield due to the trap states on their surfaces. The oxide shell in the core-shell nanomaterials based on cores such as CdSe serves to provide an inert protective barrier on the nanoparticle surfaces and to introduce new properties to core-shell structure [6]. CdSe/ZnO core-shell nanoparticles were prepared by adding zinc acetate and lithium hydroxide into CdSe nanocrystals dissolved in ethanol under ultrasonic at low temperatures [7, 8]. XRD results showed CdSe nanocrystals were prepared in the hexagonal phase which minimized lattice mismatch between CdSe and ZnO.

The UV-Vis absorption maximum of CdSe/ZnO core-shell material showed a minor red shift from that of bare CdSe nanocrystals and there was an increased fluorescent intensity when ZnO nanomaterial passivated on the surface CdSe nanocrystals.

Zinc oxide is one of the important shell-forming materials because of its wide band gap, it is known to be nontoxic, biosafe, and biocompatible [9], and it can be easily prepared through chemical solution processes including sol-gel [10], hydrothermal synthesis [11], and electrochemical deposition [12]. ZnO is a versatile material and has been used for its catalytic, electrical, optoelectronic, and photochemical properties [13]. In this work, we report on the synthesis and characterization of thioglycerol-stabilized CdSe/ZnO core-shell nanoparticles prepared by the aqueous route. The core and core-shell Materials were characterized for their optical properties by the UV-Visible (UV-Vis) spectrophotometry and photoluminescence (PL). Transmission electron microscopy (TEM) was used to determine the size and morphology of the core and core-shell Materials. To our knowledge, there have been very few reports on CdSe capped with ZnO Material in the literature [7, 8].

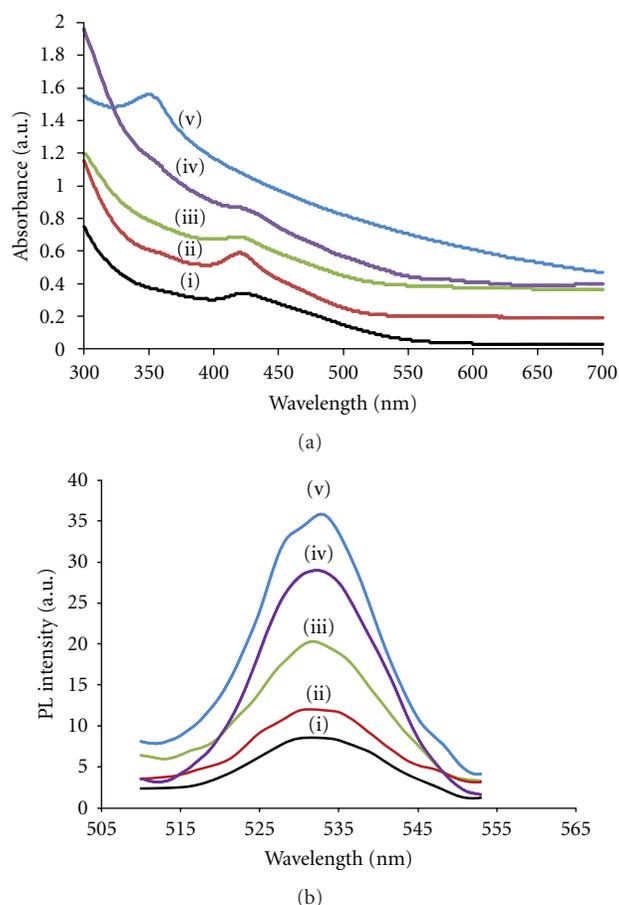
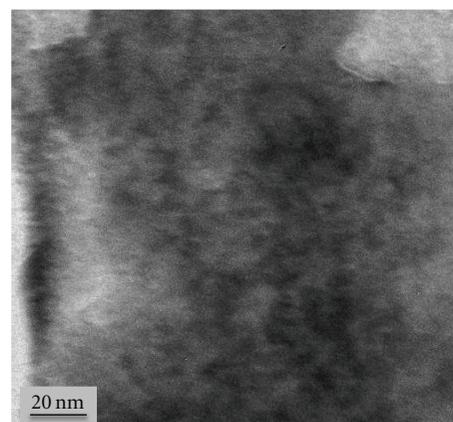


FIGURE 1: (a) Absorption spectra and (b) emission (PL) spectra for CdSe core (i) and CdSe/ZnO CS NP prepared with (ii) 2.5, (iii) 5.0 (iv) 25, and (v) 50 mL of 0.05 M zinc nitrate.

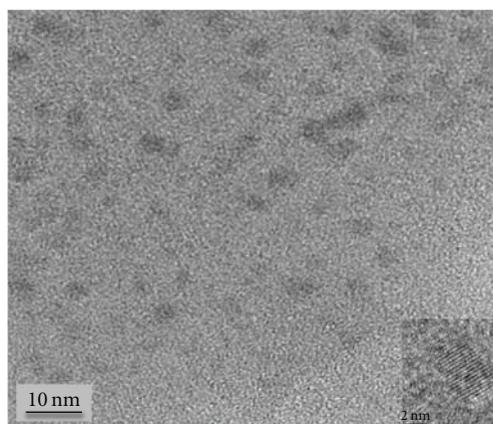
2. Methods

2.1. Chemicals. The following chemicals, 1-thioglycerol (TG) (98%), sodium borohydride (NaBH_4) (98.5%), selenium powder (Se) (99.5%, 100 Mesh), and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99%) were purchased from Sigma-Aldrich. Cadmium chloride (CdCl_2) (55-56%) was purchased from Reidel-De Haën, and sodium hydroxide (NaOH) was obtained from Merck. All these chemicals were used as received, without any further purification.

2.2. Instrumentation. UV-Visible spectra were recorded at room temperature with a Shimadzu UV-2450 (PC) S spectrophotometer. Photoluminescence spectra were measured on the colloidal solution at room temperature with Perkin Elmer LS 45 fluorescence spectrometer at the excitation wavelength of 400 nm. TEM images were recorded on both the HITACHI JEOL 100S operated at 80 kV and TECNAI G^2 SPIRIT TEM operated at 120 kV by casting one drop of a sample on carbon-coated copper grids and allowing the sample to dry room temperature. EDS analysis was done on TECNAI G^2 SPIRIT TEM instrument. Powder X-ray diffraction



(a)



(b)

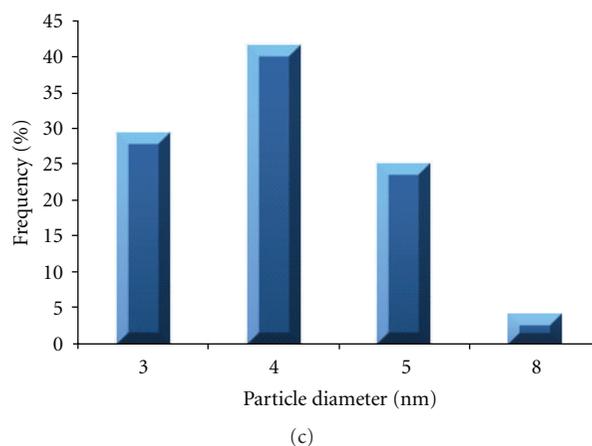


FIGURE 2: (a) TEM, (b) HMTEM images, and (c) size distribution for CdSe particles in image (b) for thioglycerol-stabilized CdSe core nanoparticles.

measurements were performed on Bruker D9 X-ray diffractometer using $\text{CuK}\alpha$ (1.5406 \AA) radiation operated at 40 kV and 40 mA.

2.3. Synthesis of CdSe and CdSe/ZnO Core-Shell Nanoparticles. The methodology for the synthesis of colloidal CdSe nanoparticles in aqueous phase was adopted from

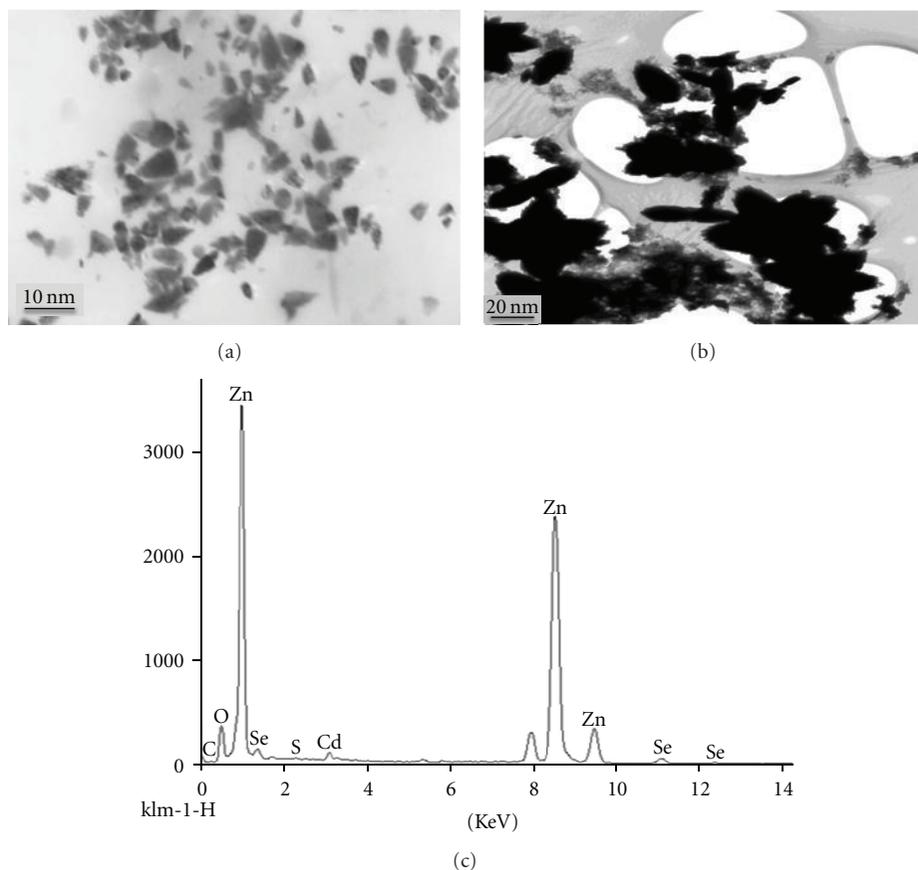


FIGURE 3: TEM image for CdSe/ZnO core-shell nanoparticles prepared with 50 mL (a) and 25 mL (b) of 0.05 M zinc nitrate and the EDS spectrum (c) for a 50 mL $\text{Zn}(\text{NO}_3)_2$ solution.

Oluwafemi et al. [14], with minor modifications. Solution A which was a stock solution of selenium precursor was prepared by dissolving 0.81 mmol of sodium borohydride in 20 mL deionised water under vigorous magnetic stirring and inert atmosphere. To the above solution was added 0.32 mmol of selenium powder, and the mixture was continuously stirred for 2 hours at room temperature. A colourless sodium hydrogen selenide solution (NaHSe) was obtained.

Solution B was prepared by adding 1 mL of cadmium chloride solution (16×10^{-3} M) to 20 mL deionised water in 250 mL three-necked round bottom flask followed by 2 drops of 1-thioglycerol stabilising agent at room temperature, under vigorous Magnetic stirring and inert atmosphere. The solution was adjusted to pH 11 with 0.1 M sodium hydroxide (NaOH) solution. 1 mL of NaHSe stock solution (Solution A, 16×10^{-3} M) was injected rapidly to Solution B under intense magnetic stirring, resulting in a yellow CdSe colloidal solution. The reaction temperature was raised from ambient to 60°C and maintained at this temperature for 30 minutes. Heat source was removed and the colloidal CdSe solution was filtered by gravity to remove unreacted Material.

In the preparation of CdSe/ZnO core-shell nanoparticles, the volume of 0.05 M zinc nitrate precursor varied from 2.5, 5, 25 and 50 mL, respectively, were slowly added to 20 mL CdSe colloidal solution under vigorous magnetic stirring

and inert atmosphere. The resulting solution was slowly adjusted to pH 12 with 0.1 M NaOH solution. The reaction temperature was maintained at 40°C for 5 minutes.

3. Results and Discussion

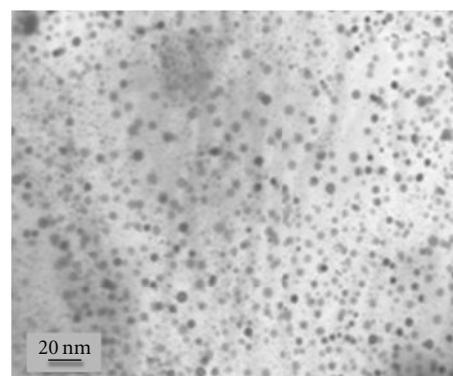
3.1. Absorption and Emission Spectra. Figure 1(a) depicts UV-Visible absorption spectra obtained for CdSe/ZnO core-shell prepared with 0.1 M NaOH and varying the volumes (2.5, 5, 25, and 50 mL) of 0.05 M zinc nitrate solution as shell precursors. CdSe core shows a 1s-1s transition peak centred at ~ 425 nm [5, 15, 16]. The particles are blue-shifted from 712 nm band gap of the bulk CdSe to 560 nm, which is strong evidence for quantum confinement [17]. The 1s-1s absorption peak was broadened when the volume of zinc nitrate was increased from 2.5 mL to 25 mL, and the absorption edge red-shifted with respect to the absorption spectra for CdSe core nanoparticles. This observation is due to the increase in particle sizes as a result of the formed core-shell nanoparticles [5, 15]. The CdSe absorption peak completely disappeared when 50 mL of 0.05 M zinc nitrate solution was used for shell growth on the surface of CdSe core nanoparticles, with only the absorption peak for ZnO nanoparticles observed at ~ 354 nm (Figure 1(a)). The dominance of the zinc oxide feature is a result of excess

zinc ions which precipitated in the solution as free ZnO nanocrystals upon addition of sodium hydroxide.

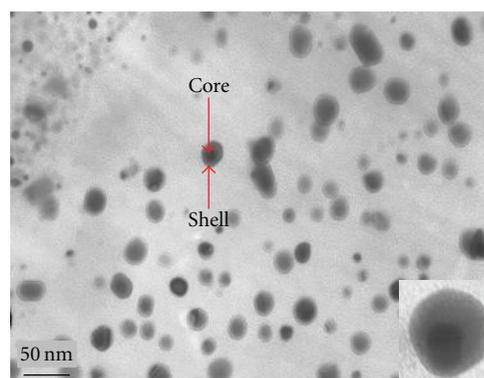
Figure 1(b) depicts photoluminescence spectra for core-shell nanoparticles prepared with different volumes of 0.05 M zinc nitrate solution which ranged from 2.5 mL to 50 mL. Bare CdSe core nanoparticles show a PL Maximum at 531 nm. An increase in the volume of the shell precursor from 2.5 mL to 50 mL resulted in the increase in the PL intensity as shown in Figure 1(b). However, the PL Maximum was slightly red-shifted to 535 nm and broadened with 50 mL of zinc nitrate shell precursor. ZnO nanoparticles generally exhibit the emission peaks in the 500–600 nm range [18–20]. The increased PL intensity is a result of decreased surface defects caused by the ZnO coating on the surface of CdSe nanocrystals [7, 8], and the broadening of the PL peak is due to the large-size distribution of the particles and the overlap of CdSe and ZnO emission peaks present in the solution samples prepared with 25 mL and 50 mL of zinc nitrate shell precursor solution.

3.2. Transmission Electron Microscopy. Figure 2 shows TEM and HMTEM images as well as particle size distribution for the CdSe-core nanoparticles. The low-resolution TEM shows a well-dispersed arrangement of the prepared thioglycerol-stabilized CdSe nanoparticles (Figure 2(a)). However, HMTEM image in Figure 2(b) reveals the Morphology of the CdSe particles are nearly spherical, and the existence of lattice planes of the nanoparticles shown in the inset in Figure 2(b) confirm CdSe nanoparticles are crystalline. The size distribution of CdSe NC is shown in Figure 2(c) and reveals average particle diameter of 4.3 nm with standard deviation of 1.398 nm.

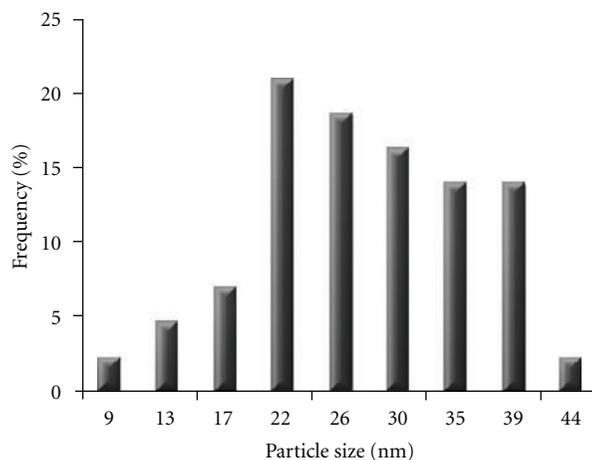
Precipitation of zinc oxide shell on the surface of CdSe core nanoparticles with 50 mL zinc nitrate solution (0.05 M) and adjusting the solution to pH 12 with 0.1 M sodium hydroxide solution produced isolated zinc oxide nanoparticles. The existence of zinc oxide nanoparticles in the sample is evident from the nanotriangle and the flower morphology of the particles depicted in Figures 3(a) and 3(b) as well as the appearance of the absorption peak at ~ 354 nm in Figure 1(a). The nanotriangle Morphology of ZnO NCs is a known phenomenon [20]. However, the EDS spectrum depicted in Figure 3(c) for the nanotriangle Morphology shows the presence of Cd and Se elements due to CdSe as well as Zn and O for ZnO Material. Thioglycerol which was used as a capping agent is the source of sulfur detected by EDS. Spherical CdSe/ZnO core-shell nanoparticles were obtained when 5 mL of 0.05 M zinc nitrate solution was used as shell precursor. The particles are depicted in Figure 4(a), and a higher magnification of the particles is shown in Figure 4(b). Core-Shell particles are clearly visible in Figure 4(b) which is characterized by a darker CdSe core particles passivated on their surfaces by a lighter ZnO shell Material. The size distribution of the CdSe/ZnO core-shell nanoparticles ranged from about 10 to 45 nm in diameter with the average size of 28 nm as shown in Figure 4(c).



(a)



(b)



(c)

FIGURE 4: TEM images for the TG-capped CdSe/ZnO CS NPs prepared with 5 mL 0.05 M zinc nitrate under different Magnification 50 K (a), 100 K (b), and particle size distribution.

3.3. X-Ray Diffraction Analysis. The XRD pattern in Figure 5 reveals that thioglycerol-capped CdSe NCs prepared under our conditions precipitated in the face-centred cubic phase. It is characterized by the strong peak intensities identified as (111), (220), and (311). The XRD peaks in Figure 5 are broad, which is an indication that particles of the CdSe NCs are small.

Figure 6 shows XRD patterns for CdSe/ZnO core-shell nanoparticles prepared with different volumes (5 mL, 25 mL,

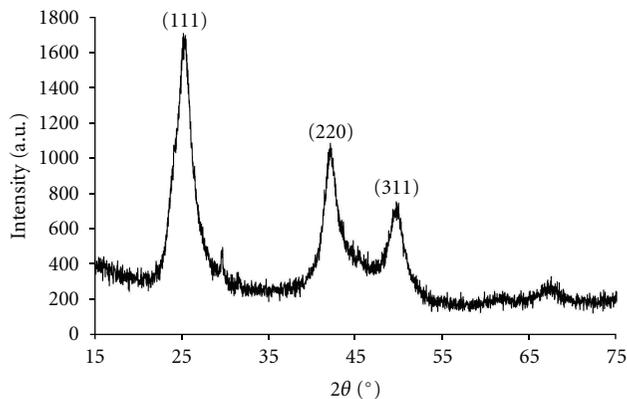


FIGURE 5: XRD patterns for thioglycerol-capped CdSe core NCs.

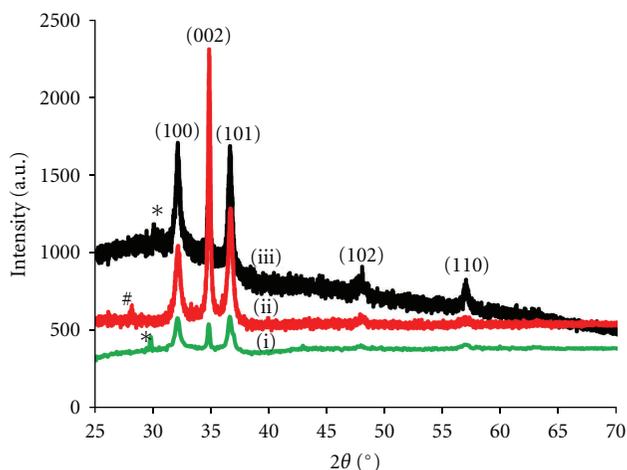
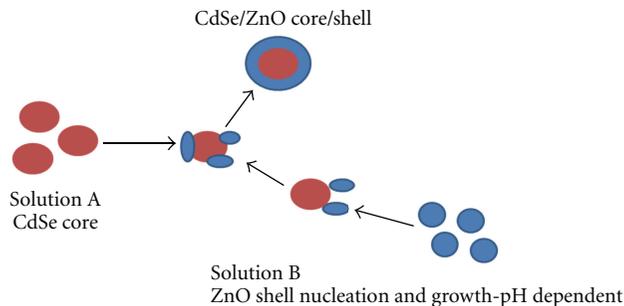


FIGURE 6: XRD patterns for CdSe/ZnO NPs prepared with (i) 5 mL, (ii) 25 mL, and (iii) 50 mL of 0.05 M zinc nitrate solution. (* and # represent Zn(OH)₂ impurity peaks).

and 50 mL) of the shell precursor, 0.05 M zinc nitrate. The (100), (002), (101), (102), and (110) XRD peaks indicate the presence of ZnO wurtzite structure. It can clearly be seen that the peak intensities are more enhanced with increasing volumes of the shell precursor, confirming the presence of more ZnO nanoparticles. No CdSe peaks were detected for all the core-shell samples shown in Figure 5. It could be due to either low amount of CdSe present in the core-shell structure or low peak intensities. The presence of Zn(OH)₂ impurity peaks was detected in both samples and was marked by the asterisks (*) and (#).

The formation of the core-shell is thought to be sequential with core, CdSe forming first, and subsequently the precipitation of ZnO which is from solution B nucleate and grows on the surface of the core (Scheme 1). CdSe core serves as seeding for the nucleation and growth of ZnO particles can be controlled. The formation of the spherical core-shell nanomaterials can be achieved at lower concentration which in this work was 5 mL of 0.05 M of zinc salt, compared to larger volume of the salt such as 25 and 50 mL.



SCHEME 1: Diagram showing the mechanism of CdSe/ZnO core-shell nanomaterial growth.

4. Conclusions

CdSe/ZnO core-shell nanomaterials prepared by varying the amount of precursor volumes showed gradual change with particles and composition as observed from the absorption and emission features as well as EDS from their TEM analysis. The core-shell features are well defined when a volume of 5 mL of 0.05 M Zn²⁺ ions are used. The spherical core-shell structures are observed when 5 mL of zinc nitrate solution was added with more star shapes forming as more ZnO nanoparticles are introduced. The result is a Mixture of spheres and stars indicating excess of ZnO as evident from the XRD analysis.

Acknowledgments

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